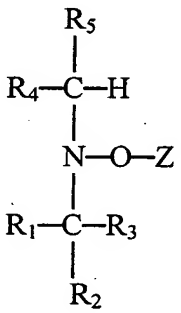
The subject matter which applicants regard as their invention is particularly pointed out and distinctly claimed as follows.

We claim:

1. A process for the controlled free radical solution polymerization to a level of solids suitable for use as low volatile organic solvent coating compositions while maintaining viscosity suitable for such coatings of monomers comprising substituted or unsubstituted acrylic acid, or esters thereof in a solvent suitable for high solids coating application at a monomer concentration sufficient to give the desired polymer concentration which comprises treating said monomers in said solvent with a controlled free radical initiator selected from the group N,N-dialkyl-alkoxyamines having one hydrogen atom on one carbon atom in the α position of one alkyl group attached to the amino nitrogen, nitroxyl radicals having one hydrogen atom on one carbon atom in the α position of one alkyl group attached to the nitroxyl nitrogen and mixtures thereof.

2. A process as defined in claim 1 wherein the alkoxyamine has the structure II:

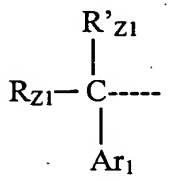


(II)

Wherein R_1, R_2, R_3, R_4,and R_5 are independently selected from the group consisting of straight chain alkyl, branched chain alkyl and cyclic alkyl, substituted, or unsubstituted aralkyl, and substituted or unsubstituted aryl groups having from 1 to 50 carbon atoms, with the proviso that one of said R moieties be substituted with, or contain sulfur, or phosphorous and any two of R_1, R_2, R_3, R_4 and R_5 which do not contain sulfur, or phosphorous, and which are attached to the same carbon atom, may be concatenated to form, when taken together with the carbon atom to which they are attached, a cyclic alkyl group of from 5 to 20 carbon atoms and Z is selected from

the following groups, wherein the dashed line attached to the carbon atom represents either a free electron or the point of attachment to the oxygen atom of the original alkoxyamine as appropriate:

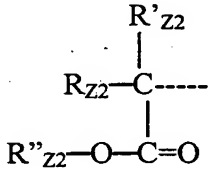
a benzylic radical of the general formula Z1:



(Z1)

wherein Ar_1 is an aryl group which may be substituted with halogen atoms, hydroxyl, alkoxy, ester, carboxy, acyl, amino, nitro, cyano, amido, sulfonyl, or phosphonyl groups and where R_{Z1} and R'_{Z1} are independently selected from hydrogen atoms, or cyclic alkyl, straight chain alkyl, or branched chain alkyl groups, of from 1 to 50 carbon atoms and which alkyl groups may be unsubstituted or substituted with any of the above named substituent groups for Ar_1.

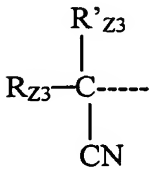
an ester type radical of general formula Z2:



(Z2)

Wherein R_{Z2}, R'_{Z2} and R''_{Z2} are independently selected from straight chain alkyl, branched chain alkyl or cyclic alkyl groups of from 1 to 50 carbon atoms which alkyl groups may be unsubstituted or substituted with any of the above defined substituents for Ar_1 and R''_{Z2} may also be hydrogen.

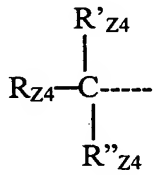
a cyano radical of the general formula Z3:



(Z3)

wherein R_{Z3} and R'_{Z3} are independently selected from cyclic alkyl, straight chain alkyl, or branched chain alkyl groups of from 1 to 50 carbon atoms which alkyl groups may be unsubstituted or substituted with any of the named substituent groups for Ar_1 and

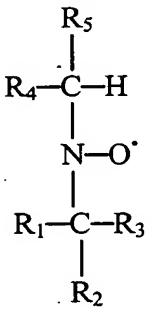
an alkyl radical of the general formula Z4:



(Z4)

wherein R_{Z4}, R'_{Z4} and R''_{Z4} are independently selected from among the alkyl groups as defined for R_{Z3}.

3. A process as defined in claim 1 wherein the nitroxyl radical has the structure I:



(I)

wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from the group consisting of straight chain alkyl, branched chain alkyl, cyclic alkyl, substituted, or unsubstituted aralkyl, or substituted, or unsubstituted aryl groups having from 1 to 50 carbon atoms, with the proviso that one of said R moieties be substituted with, or contain sulfur or phosphorous and any two of R_1, R_2, R_3, R_4 and R_5 which do not contain sulfur, or phosphorous, and which are attached to the same carbon atom, may be concatenated to form, when taken together with the carbon atom to which they are attached, a cyclic alkyl group of from 5 to 20 carbon atoms.

4. A process as defined in claim 1 wherein the controlled free radical initiator is an alkoxyamine selected from the group consisting of methyl 2-[N-t-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxy]propionate, 1-phenyl-1-[N-t-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxy]ethane, 1,1-dimethyl-1-[N-t-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxy]ethane, 1-methyl-1-cyano-1-[N-t-butyl-N-(1-diethyphosphono-2,2-dimethylpropyl)-N-oxy]ethane and mixtures thereof.

5. A process as defined in claim 1 wherein the controlled free radical initiator is the alkoxyamine methyl 2-[N-t-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxy]propionate.

6. A process as defined in claim 1 wherein the controlled free radical initiator comprises a mixture of alkoxyamines as defined in claim 2 and nitroxyl radicals as defined in claim 3.

7. A process as defined in claim 4 wherein the controlled free radical initiator also includes nitroxyls derived from the alkoxyamine selected from the group defined in claim 4.

8. A process as defined in claim 5 wherein the controlled free radical initiator also includes a nitroxyl radical derived from the alkoxyamine.

9. A process as defined in claim 1 also including an organic peroxide initiator or an azonitrile initiator.

10. A process as defined in claim 1 wherein the monomers comprising substituted or unsubstituted acrylic acid or esters thereof are selected from the group consisting of : (subgroup a) 2-hydroxyethyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl acrylate, 2-hydroxybutyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, 2-hydroxybutyl methacrylate, 3-hydroxypropyl methacrylate, 3-hydroxybutyl methacrylate, 4-

hydroxybutyl methacrylate, glycidyl acrylate, glycidyl methacrylate, acetoacetoxy ethyl acrylate, acetoacetoxy ethyl methacrylate and mixtures thereof,

(subgroup b) methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, lauryl acrylate and mixtures thereof,

(subgroup c) acrylic acid, methacrylic acid and mixtures thereof,

(subgroup d) iso-octyl acrylate, diethylaminomethyl acrylate, diethylaminomethyl methacrylate, t-butylaminoethyl methacrylate, t-butylaminoethyl acrylate and mixtures thereof,

with the proviso that at least one member of subgroup a and of subgroup b must be present.

11. A process as defined in claim 10 wherein a monomer selected from the group styrene, para-methyl styrene, vinyl acetate and mixtures thereof is also present.

12. A process as defined in claim 11 wherein the monomers comprise butyl acrylate, hydroxyethyl acrylate, styrene and acrylic acid.

13. A process as defined in 11 wherein the monomers comprise glycidyl methacrylate, butyl methacrylate, ethyl acrylate, methyl acrylate, methyl methacrylate, methacrylic acid, hydroxypropyl acrylate, hydroxypropyl methacrylate, acetoacetoxy ethyl acrylate, acetoacetoxy ethyl methacrylate and mixtures thereof.

14. The product produced by a process as defined in claim 1.

15. A process for coating an object on at least one surface which comprises applying a product as defined in claim 14 to said at least one surface and treating said product after application on said at least one surface to sufficient heat for a sufficient time to evaporate the solvent contained in said product and crosslink the remaining material of said product on said at least one surface.

16. The coating produced by the process defined in claim 15.

17. The coated object produced by the process defined in claim 15.

18. A process as defined in claim 1 wherein the polymer so produced is recovered as a solvent free material.

19. A powder coating material prepared from the solvent free material prepared as defined in claim 18.

20. An object coated on at least one surface thereof with a coating formed by applying the powder coating material defined in claim 19 to the said at least one surface of said object and fusing said powder coating material into a coherent coating.

21. A process as defined in claim 2 wherein one of R_1, R_2, R_3, R_4, or R_5 is $-P(=O)R_6R_7$ wherein R_6 and R_7 are independently selected from the group consisting of methyl, methoxy, ethoxy, n-propoxy, benzyloxy, dodecyloxy, phenyl and benzyl.

22. A process as defined in claim 3 wherein one of R_1, R_2, R_3, R_4, or R_5 is $-P(=O)R_6R_7$ wherein R_6 and R_7 are independently selected from the group consisting of methyl, methoxy, ethoxy, n-propoxy, benzyloxy, dodecyloxy, phenyl and benzyl.

23. A process as defined in claim 6 wherein, independently in the alkoxyamine and the nitroxyl, one of R_1, R_2, R_3, R_4, or R_5 is $-P(=O)R_6R_7$
wherein R_6 and R_7 are independently selected from the group consisting of methyl, methoxy, ethoxy, n-propoxy, benzyloxy, dodecyloxy, phenyl and benzyl.

24. A process as defined in claim 2 wherein R_1, R_2 and R_3 are methyl, R_4 is t-butyl and R_5 is $-P(=O)R_6R_7$ wherein R_6 and R_7 are independently selected from straight chain alkyl, branched chain alkyl, or cyclic alkyl groups, aralkyl groups having straight chain alkyl, branched chain alkyl, or cyclic alkyl portions, straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy groups and aralkoxy groups having straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy portions and all of said groups may be unsubstituted or substituted with any functional group compatible with a nitroxyl radical.

25. A process as defined in claim 24 wherein R_6 and R_7 are linear alkoxy groups of from 1 to 20 carbon atoms.

26. A process as defined in claim 24 wherein R_6 and R_7 are ethoxy.

27. A process as defined in claim 3 wherein R_1, R_2 and R_3 are methyl, R_4 is t-butyl and R_5 is $-P(=O)R_6R_7$ wherein R_6 and R_7 are independently selected from straight chain alkyl, branched chain alkyl, or cyclic alkyl groups, aralkyl groups having straight chain alkyl, branched chain alkyl, or cyclic alkyl portions, straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy groups and aralkoxy groups having straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy portions and all of said groups may be unsubstituted or substituted with any functional group compatible with a nitroxyl radical.

28. A process as defined in claim 27 wherein R_6 and R_7 are linear alkoxy groups of from 1 to 20 carbon atoms.

29. A process as defined in claim 27 wherein R_6 and R_7 are ethoxy.

30. A process as defined in claim 6 wherein R_1, R_2 and R_3 are methyl, R_4 is t-butyl and R_5 is $-P(=O)R_6R_7$ wherein R_6 and R_7 in the alkoxyamine and the nitroxyl are each independently selected from straight chain alkyl, branched chain alkyl, or cyclic alkyl groups, aralkyl groups having straight chain alkyl, branched chain alkyl, or cyclic alkyl portions, straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy groups and aralkoxy groups having straight chain alkoxy, branched chain alkoxy, or cyclic alkoxy portions and all of said groups may be unsubstituted or substituted with any functional group compatible with a nitroxyl radical.

31. A process as defined in claim 30 wherein R_6 and R_7 are linear alkoxy groups of from 1 to 20 carbon atoms.

32. A process as defined in claim 30 wherein R_6 and R_7 are ethoxy.